Adsorption Efficacy of Polymerized Seed Composite for Remediation of Heavy Metals and Physico-Chemical Parameters of Water

A
Synopsis
Submitted for the Award of Degree of
Doctor of Philosophy
in
Chemistry

By

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ORIGIN OF THE PROBLEM:

Sustainable development is a process to achieve environmental protection goals, maintaining the quality of natural resources. Among various natural resources, the quality of water is of vital concern for mankind since it is directly linked with human welfare. Today, water ecosystem is facing a serious challenge to sustainable progress particularly for developing countries. To prevent this catastrophe, a wide number of technologies have been developed for water decontamination which includes electrochemical treatment, chemical precipitation, reverse osmosis, ion exchange and electro dialysis, etc. These techniques, however, are associated with several limitations like cost- prohibitive, in-effective in low and high metal concentration, generation of toxic sludge and most important is the wastage of 80 to 85% water. Such issues have boosted the research for alternative methods for water purification.

INTRODUCTION:

People need water to survive. Therefore, competition for a clean and hygienic supply of water to sustain life is intensifying day by day. The problem of water scarcity has worsened by the population explosion and water pollution. In-spite of being known as a '**blue planet**', the earth is devoid of clean, safe and hygienic water for drinking and other purposes. The crisis is basically expanded by the ways, we handle water. Today, it is a topic of great concern. In India, the situation is bitter. A large number of people in our country are unable to access clean and hygienic drinking water. A recent appraisal by Water Aid (International Organization Effective for Water Sanitation and Hygiene) illustrates that majority of surface water in India is polluted. Compounds entering in water by natural routes may be considered essential but those as a result of man-made activities are harmful to life. These life-spoiling compounds are known as **Water Pollutants**. Water pollutants have been classified in eight major categories (fig 1).

Indian population is getting affected by unsafe water contaminated with mainly toxic heavy metals like arsenic, cadmium, lead, chromium, nickel and organics. Among all the water pollutants, heavy metals are

most important because of their non-biodegradable nature. Heavy metals are active member of dirty dozen clubs of water pollutants, encountered in various ecosystem of environment. These toxic metals have been designated as **Priority Pollutants** by the US Environmental Protection Agency. They accumulate in living tissues through food chain which has human beings at its top. The characteristics, environmental concentrations, natural and anthropogenic sources, health effects and national and international standards, guidelines have been thoroughly reviewed in voluminous manner in the literature (Jaishankar et al., 2014).

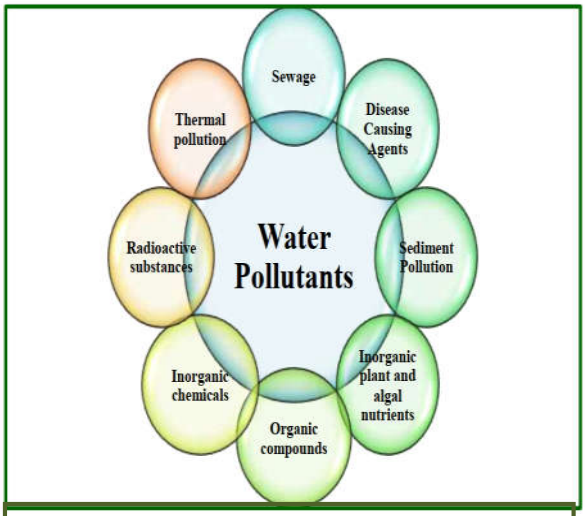


Figure 1 Classification of water pollutants

Various methods used for remediation of water have been tabulated as follows (table1)

Table 1: Conventional techniques used for water remediation

Techniques	Particulars
Ion Exchange	Heavy metals are exchanged with the corresponding ions of similar charge held on the exchange resin/surrounding material by electrostatic forces.
Chemical Precipitation	Chemicals are added in water to form insoluble metal precipitates. Resultant precipitates are cleaned out either by sedimentation or filtration. Hydroxide/ sulphide precipitation is very commonly used by industries to remove heavy metals up to ppm levels.
Membrane Filtration	The process separates heavy metal ions from contaminated water by passing it through different types of membranes that permits some ions to pass while blocking others based on the size and selectivity of membrane pores.
Coagulation	Coagulation is responsible to destabilize the colloids by neutralizing the forces on addition of a coagulant.
Flocculation	Flocculation is responsible to bind particles into large lumps. Ferric chloride and polyaluminium chloride as coagulants while mercaptoacetyl chitosan as flocculent are particularly used for heavy metals.
Adsorption	It is the ability of materials to accrue heavy metals from water by physico-chemical pathways. The process is flexible in design and operation. The effluent produced is of high-quality.

Techniques	Particulars *Contd.*
Electrochemical Treatment	It involves plating-out of metal ions on the surface of a cathode. Established techniques like electro-coagulation, electro-flotation and electro-deposition are grouped in this category.
Phyto-remediation	Selected plants are used to clean up contaminated water. It is the natural aptitude of certain plants to bio-accumulate or degrade harmful metal contaminants of water.
Biological Treatment	This process involves the use of either dead or alive microorganisms which accumulate heavy metals.

(Source: Mehta and Gaur, 2001; Kim et al. 2004; Alvarez et al., 2007; Fu and Wang, 2011)

Use of plant bio-materials with an aim to purify the water for the extension of water supply has emerged as an efficient, cost effective, eco-friendly and sustainable method. Regeneration of the biomaterial increases the cost effectiveness of the process thus, warrants its future success. Intensive research on plant mediated water purification has established solid base of knowledge, principles and highlighted enormous potential of its **commercialization**. Use of unused plant resources, exhibiting natural ability of adsorption has been considered highly effective green remediation process. Several nano-functionalized biomaterials are proved to be idealistic but possess side effects and finally impracticable for commercialization. The highest priority of commercially available remediation technology is the commercial potential, practicability, market size, cost and its maintenance.

PRESENT STATE OF KNOWLEDGE:

SEED BIOMASS: SUITABLE PROTEINACEOUS BIOMATERIAL

Among the various parts of the plant, seeds find important place for water purification being highly proteinaceous in nature. Such biomaterials have high concentration of amino acids and thus have variety of structurally related pH dependent properties of generating appropriate atmosphere for attracting the cationic and anionic species of water pollutants such as metal ions, ionic dyes and charged biomolecules. Research attempts have been made towards seed biomass for decontamination of toxic metals from water bodies (table 2).

Table 2: Seed Biomass used for metal removal

Seed Biomass	Metal Removed	References
Groundnut seeds & Sesame seed	Cu(II)	Kumar et al., 2019
Adenanthera pavonina seeds	Pb(II), Cd(II)	Sen et al., 2018
Malpighia emarginata seeds	Cd(II), Cr(III), Cu(II), Pb(II), Ni(II), Zn(II)	Souza et al., 2018; Silva et al., 2018
Nigella sativa seeds	Pb(II)	Addala et al., 2018
Coriandrum Sativum seeds	Cu(II)	Kadiri et al., 2018
Adansonia digitata seeds	Cu(II)	Adewale & Pereira, 2018
Capsicum annuum seeds	Cd(II), Pb(II)	Medellin-Castillo et al., 2017
Citrus Limettioides seeds	Ni(II)	Sudha et al., 2015
Mango seeds	Cu(II)	Ashtikar & Parkhi, 2014
Tamarindus indica seeds	Cr(VI)	Mathew et al., 2013
Moringa oleifera seeds	Pb(II), Cu(II), Cd(II), Cr(III), Cr(VI), Ni(II),As(III), As(V)	Ravikumar & Sheeja, 2013; Sharma et al., 2007, 2006; Kumari et al., 2006, 2005
Litchi chinensis seeds	Ni(II)	Flores-Garnica et al., 2013
Polyalthia longifolias seeds	Cd(II)	Rao & Rehman, 2012
Caria papaya seeds	Mn(II), Pb(II), Cu(II)	Egila et al., 2011; Hadi et al., 2011
Caesalpinia bonducella seeds	Ni(II)	Gutha et al., 2011
Leucaena leucocephala seeds	Cu(II)	Patil et al., 2010
Strychnos potatorum seeds	Pb(II)	Jayaram et al., 2009
Prosopis juliflora seeds	Pb(II)	Jayaram & Prasad, 2009
Raw date pit seeds	Cd(II)	Kahraman et al., 2008
Soursop seeds	Cu(II), Ni(II), Zn(II), Pb(II)	Oboh et al., 2008

FUNCTIONALIZATION ONTO BIOMASS:

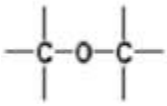
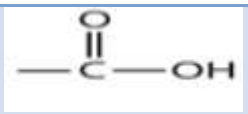
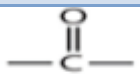
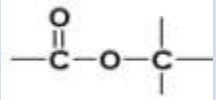
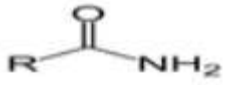
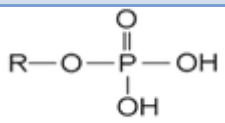
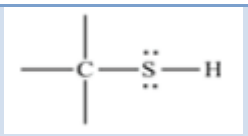
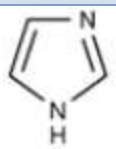
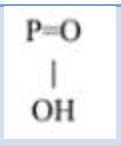
Successful attempts have been made to enhance the adsorption efficiency of biomaterials using synthetic strategies for the enrichment of active functional groups through various types of functionalization (table 3). These functionalizations are supposed to provide a better surface area for the electrostatic interaction between the adsorbate and the adsorbent.

Table 3: Modifications onto Biomass

Biomass	Types of Modifications	Modification Agents	References
Seeds	Esterification of *Ocimum basilicum* seeds	Succinic anhydride	Lodhi et al., 2019
	Surface modification onto *Adansonia digitata* seeds	EDTA	Adewale & Pereira, 2018
	Modified *Caryotaurens* seeds	Sulfuric acid	Saravanan et al., 2017
	Functionalization on mango seeds shell powder	EDTA	Moyo et al., 2017
	Functionalized *Adansonia digitata* seeds	Nitrilotriacetic acid	Adewale & Pereira, 2016
	Modified avocado seeds	Sulfuric acid	Bhaumik et al., 2014
	Modified *Leucaena leucocephala* seed powder	Polyethylenimine	Raj et al., 2012
	Graft copolymerization on guava seeds`	Monomethylolthiourea	Zewail et al., 2010
Cellulose	Functionalised cellulose	Glycidyl Methacrylate	Varshney et al., 2018
	Esterification of cellulose	EDTA	d'Halluin et al., 2017
	Grafting on cellulose	Itaconic Acid	Varshney et al., 2016
	Amine-modification cellulose	Humic acid	Jebali et al., 2015
	Thiolation on cellulose	Aminoethanethiol	Silva et al., 2013
	Sulfonation on cellulose	Divinylsulfone	Yu et al., 2012
Stem Fiber	Grafting on banana stem fiber	Poly(methacrylic acid)	Salamun et al., 2016
	Modified Aloe vera	Phosphoric acid	Malik et al., 2015
	Modified ramie fiber	EGTA	Sun et al., 2014
	Modified juniper fibre	Sodium hydroxide	Min et al., 2004
Husk	Modified De-Oiled Allspice	Nitric acid , ethanol	Cruz-Olivaresaet al., 2010
	Modified groundnut husk	Sulfuric acid /silver	Dubey& Gupta, 2007
	Modified rice husk	Tartaric acid	Wong et al., 2003
Sawdust	Modified cedrus deodar wood	Sodium hydroxide	Memon et al., 2007
	Modified Oak tree	Hydrochloric acid	Argun et al., 2007
	Modified walnut	Formaldehyde	Bulut & Tez , 2003
Miscellaneous	Grafting of tea waste	Polyacrylic acid	Awadallah-F et al., 2017
	Graft copolymerization on bagasse	Acrylonitrile	Niu et al., 2014
	Xanthation of bagasse	Xanthic acid	Homagai et al., 2010
	Modified Cassava waste	Thioglycollic acid	Abia et al., 2006
	Modified bagasse fly ash	Hydrogen peroxide	Gupta & Ali, 2004

Following functional groups in plant material have been found responsible for binding (table 4).

Table 4: Functional groups responsible for binding between adsorbate and adsorbent

Formula of Functional Group	Name	Ligand Atom	Class of Compound
R – OH	Hydroxyl	O	Alcohol, carbohydrate, phenols
	Etheric	O	Ether, polysaccharides
	Carboxylic	O	Fatty acids, Proteins, Organic acids
	Carbonyl group	O	Aldehydes, carbohydrates
	Ester	O	Lipid, oils
	Amide	N	Proteins
=NH	Imine	N	Amino acids
	Phosphate	O	DNA, RNA, ATP
	Thiols	S	Cysteine, amino acids
	Imidazole	N	Amino acids
	Phosphodiester	P	Teichoic acid

(Source: Al-Qodah et al., 2017)

LACUNAE IN THE KNOWLEDGE:

In the provision of cleaning of water, the quantity of main water pollutants like toxic metals, are not only the culprits. Besides their presence, increased level of turbidity, hardness, conductivity and TDS are also harmful for living organisms. Various national and international standards were set for water to be used for different purposes. In spite of strict environmental protection legislations and public environmental concerns, water pollutants and related parameters are posing serious peril to the environment worldwide especially in developing countries. A vigorous survey of the literature on the topic indicates that different plant mediated materials have been used for the decontamination of different primary water pollutants and related water check parameters separately. However, a little effort has been made to use a composite of different plant based materials to take overall care of water quality.

OBJECTIVES:

With this aim in view, the present research is focused towards the decontamination of toxic metals (Cd, Pb, Cr and As) along with reduction of water check parameters like pH, hardness, total dissolved solids, salinity and conductivity) exploiting the adsorption and coagulation efficiency of a composite of two seed powder (*Moringa oleifera and Leucaena leucocephala*). To enhance the bio-efficacy and stability, environmentally safe synthetic strategies of functionalization will be carried out on the native seed mixture. Reusability and Regeneration studies will also be considered to make the proposed adsorbent (seed composite) economical.

PLAN OF WORK: *AT A GLANCE*

☞ **Preparation of seed composite**

- *Moringa oleifera (Sahjan)*
- *Leucaena leucocephala (Subabul)*

☞ **Functionalization onto seed composite**

- ***Encapsulation of seed composite with PVA (enrichment of poly OH groups)***

Enrichment of anionic groups on encapsulated seed composite

for binding of cationic metals

- *Acrylic acids graft co-polymerization*
- *Itaconic acid graft co-polymerization*

Enrichment of cationic groups on encapsulated seed composite

for binding of anionic metals

- *N,N-methylene bisacrylamide graft co-polymerization*
- *Glycidyl Methacrylate graft co-polymerization*

☞ **Protein-metal interactions:** ***(to highlight mechanistic aspects of binding)***

- *Isolation and purification of protein from seeds of interest*
- *Characterization of protein bands of different molecular weights using biomarker*
- *Identification of most potent protein fraction-metal interaction using gel electrophoresis*

☞ **Batch mode Adsorption studies** ***(optimization of experimental conditions)***

Optimization of the experimental conditions will be carried out as a function of

- *Biomass dosages*
- *Contact time*
- *Metal concentration*
- *Volume of test solution*
- *pH*
- *Temperature*

☞ **Batch mode Coagulation studies for reduction of water quality parameters** ***(optimization of experimental conditions)***

- *pH*
- *Hardness*
- *TDS*

- *Salinity*
- *EC*

☞ **Equilibrium modeling and thermodynamic studies** ***(to evaluate adsorption capacity in mg/g, information of academic interest and the feasibility of sorption process in the environmental conditions)***

Equilibrium modeling

- *Langmuir isotherm*
- *Freundlich isotherm*
- *Dubinin-Radushkevich isotherm*
- *Temkin isotherm*

Adsorption thermodynamic

- *Gibbs free energy (ΔG^0)*
- *Enthalpy (ΔH^0)*
- *Entropy (ΔS^0)*

☞ **Regeneration and Reusability** ***(to evaluate cost effectiveness on the basis of number of desorption cycles required for complete desorption of loaded metal and how many times it can be reused cycles)***

Sorption-desorption cycle of biosorbent using various types of eluants

MATERIALS AND METHODS:

Seeds Composite:

A mixture of seed powder of two plants (*Moringa oleifera and Leucaena leucocephala*) will be used as biosorbent. The details of these plants are as follows:

A. *Moringa oleifera* (Sahjan)

Moringa oleifera is the most widely cultivated species full of nutrients and vitamins and it is good as a food. It is used as a primary coagulant in drinking water clarification and waste water treatment. It is also

a useful source for medicines. Laboratory investigations confirm that the *Moringa* seeds are highly effective in the removal of suspended solids and also have the capability to clean the turbid water.

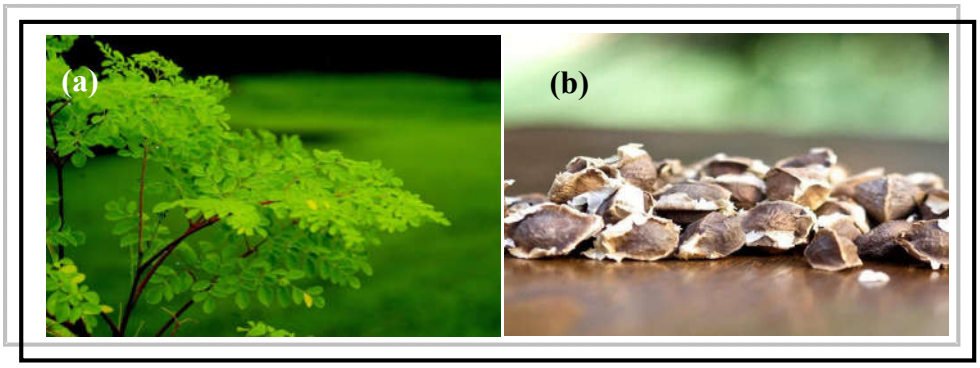


Figure 2: *Moringa oleifera* (a) plant and (b) seeds

CLASSIFICATION

Kingdom: Plantae

Order: Brassicales

Family: Moringaceae

Genus: *Moringa*

Species: *oleifera*

Binomial name: *Moringa oleifera*

CHEMICAL COMPOSITION

Fat	16.7g
Proteins	31.4g
Carbohydrates	18.4g
Fiber	7.3g
Ash	6.2g
Moisture	2.0g

(Per 100g) on dry weight basis

Amino acid composition (g Amino acid/100g protein), contents of Moringa oleifera seed powder

Amino Acids	AA composition (g AA/ 100g protein)
Lysine	3.24
Threonine	3.22
Methionine	0.97
Valine	3.09
Isoleucine	4.35
Leucine	5.27
Phenylalanine	4.53
Histidine	2.01
Serine	4.25
Proline	2.32
Glycine	5.00
Alanine	3.23
Tyrosine	2.33
Aspartic acid	6.14
Glutamic acid	14.76
Arginine	8.06

(Source: Okereke and Akaninwor, 2013)

B. *Leucaena leucocephala* (Subabul)

Leucaena leucocephala is a tropical plant abundantly available throughout the year. It is a large shrub or a small tree to about 10 meter in height and it is mostly grown in gardens and near the villages. It is known as the **'miracle tree'** because of its worldwide success as a long-lived and highly nutritious forage tree. It is highly rich in proteins and used as a source of protein. It has no chronic effects on the humans.

Figure 3: *Leucaena leucocephala* (a) plant and (b) seeds

CLASSIFICATION

Kingdom: Plantae

Order: Fabales

Family: Fabaceae

Genus: *Leucaena*

Species: *leucocephala*

Binomial name: *Leucaena leucocephala*

CHEMICAL COMPOSITION

Fat	2.7g
Proteins	32.9g
Carbohydrates	14.4g
Fiber	6.3g
Ash	0.62g
Moisture	1.0g

(Per 100g) on dry weight basis

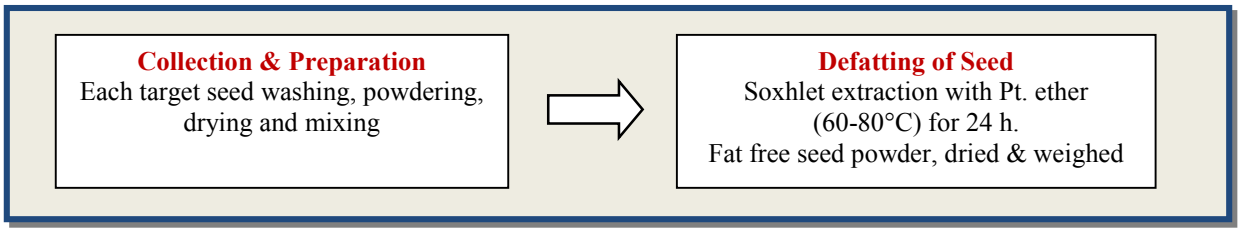
Amino acid composition (g Amino acid/100g protein), contents of Leucaena leucocephala seed powder

Amino Acids	AA composition (g AA/ 100g protein)
Lysine	4.21
Threonine	2.26
Methionine	0.85
Valine	3.02
Isoleucine	15.88
Leucine	4.84
Phenylalanine	3.02
Histidine	2.57
Serine	3.36
Proline	2.78
Glycine	3.68
Alanine	3.00
Tyrosine	2.42
Aspartic acid	6.14
Glutamic acid	11.35
Arginine	6.17

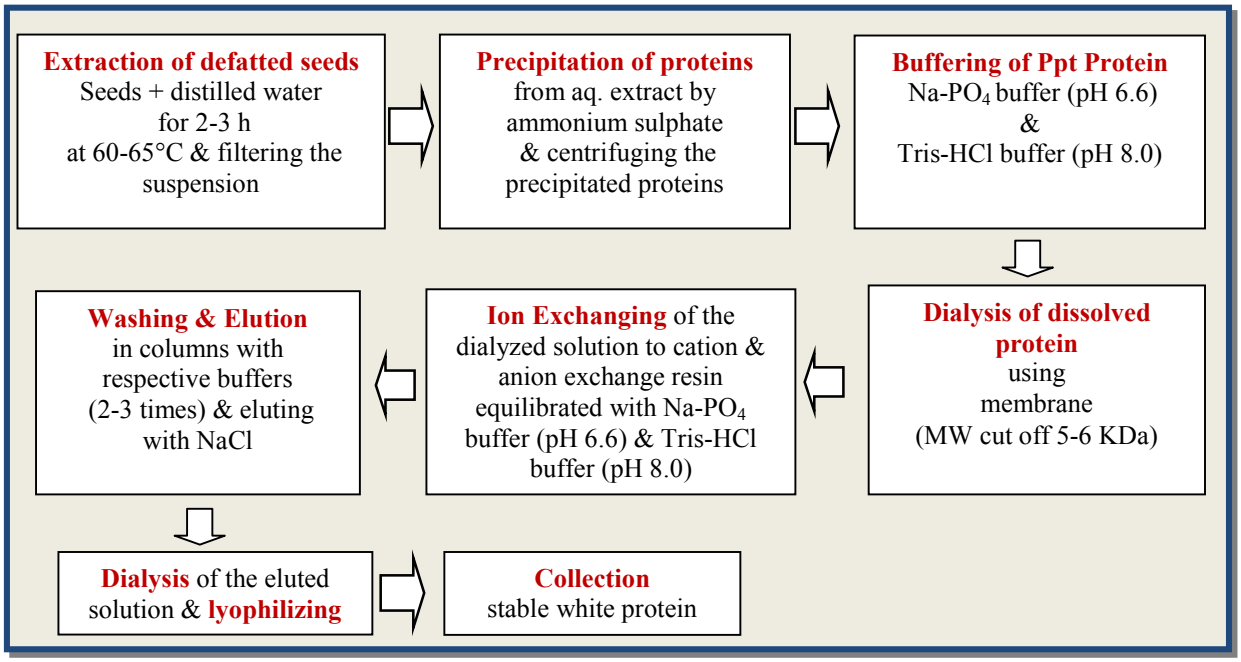
(Source: Padmavathy and Shobha, 1987)

Important experimental details are depicted schematically as follows:

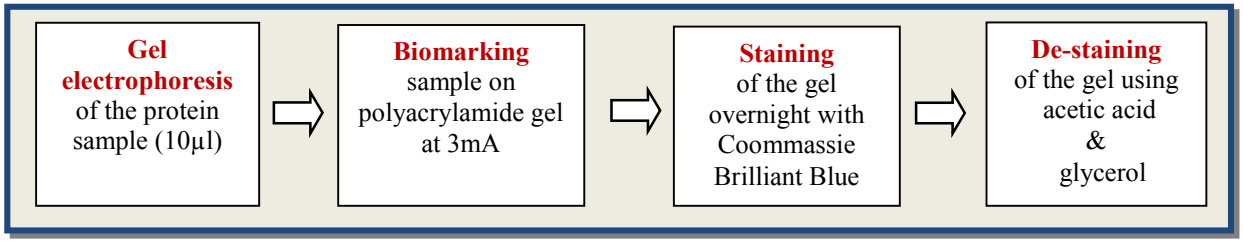
1. ***Preparation of seed composite:***


Collection & Preparation
Each target seed washing, powdering, drying and mixing
Defatting of Seed
Soxhlet extraction with Pt. ether (60-80°C) for 24 h.
Fat free seed powder, dried & weighed

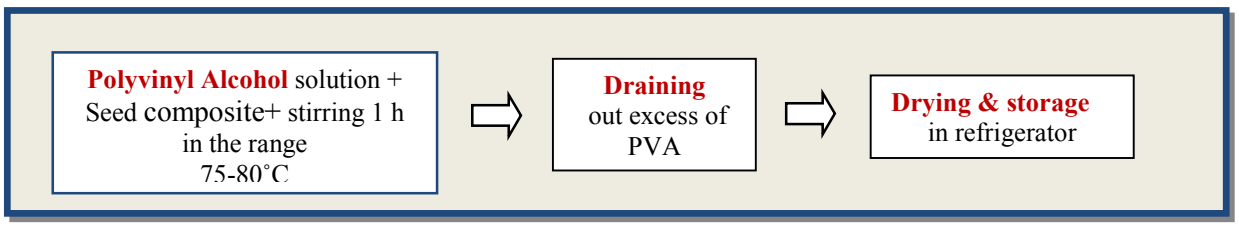
2. ***Extraction of protein from seeds:***


Extraction of defatted seeds
Seeds + distilled water for 2-3 h at 60-65°C & filtering the suspension
Precipitation of proteins
from aq. extract by ammonium sulphate & centrifuging the precipitated proteins
Buffering of Ppt Protein
Na-PO4 buffer (pH 6.6) & Tris-HCl buffer (pH 8.0)
Dialysis of dissolved protein
using membrane (MW cut off 5-6 KDa)
Ion Exchanging of the dialyzed solution to cation & anion exchange resin equilibrated with Na-PO4 buffer (pH 6.6) & Tris-HCl buffer (pH 8.0)
Washing & Elution
in columns with respective buffers (2-3 times) & eluting with NaCl
Dialysis of the eluted solution & lyophilizing
Collection
stable white protein

- ***Gel Electrophoresis:***

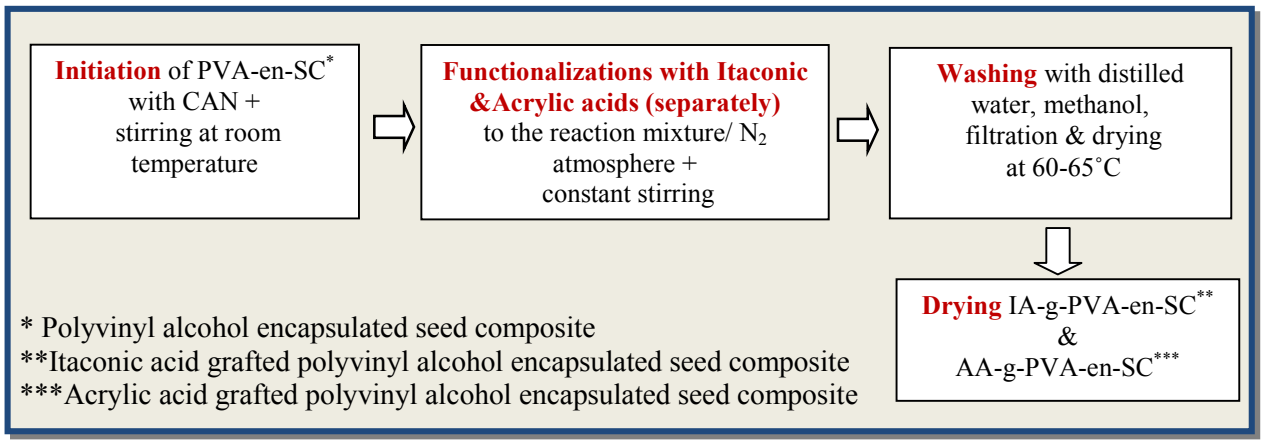

Gel electrophoresis
of the protein sample (10µl)
Biomarking
sample on polyacrylamide gel at 3mA
Staining
of the gel overnight with Coommassie Brilliant Blue
De-staining
of the gel using acetic acid & glycerol

3. ***Encapsulation onto seed composite:*** *PVA graft co-polymerization (enrichment of OH groups)*


Polyvinyl Alcohol solution + Seed composite+ stirring 1 h in the range 75-80°C
Draining
out excess of PVA
Drying & storage
in refrigerator

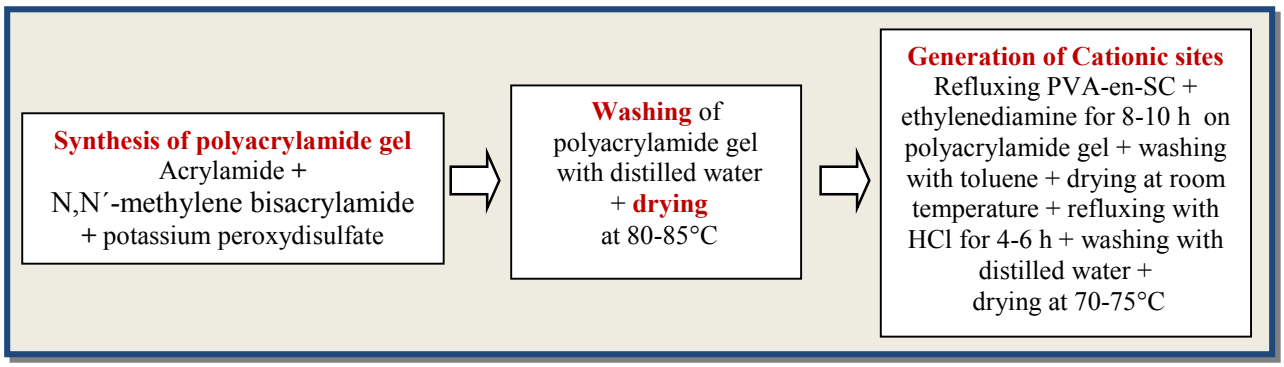
4. ***Functionalization onto encapsulated seed composite: Enrichment of anionic groups***

- ***Itaconic Acid & Acrylic Acid for binding of cationic metals***

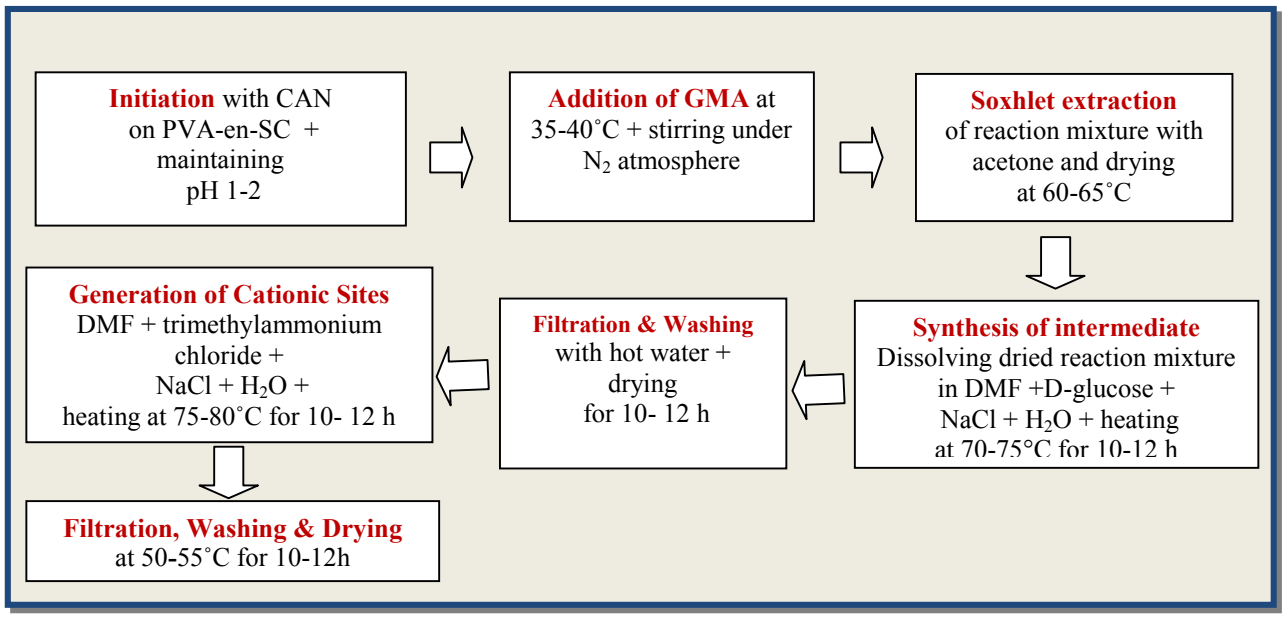

Initiation of PVA-en-SC* with CAN + stirring at room temperature
Functionalizations with Itaconic &Acrylic acids (separately) to the reaction mixture/ N2 atmosphere + constant stirring
Washing with distilled water, methanol, filtration & drying at 60-65˚C
Drying IA-g-PVA-en-SC** & AA-g-PVA-en-SC***
* Polyvinyl alcohol encapsulated seed composite
**Itaconic acid grafted polyvinyl alcohol encapsulated seed composite
***Acrylic acid grafted polyvinyl alcohol encapsulated seed composite

5. ***Functionalization onto encapsulated seed composite: Enrichment of cationic groups***

- ***N,N´-methylene bisacrylamide for binding of anionic metals***


Synthesis of polyacrylamide gel Acrylamide + N,N´-methylene bisacrylamide + potassium peroxydisulfate
Washing of polyacrylamide gel with distilled water + drying at 80-85°C
Generation of Cationic sites Refluxing PVA-en-SC + ethylenediamine for 8-10 h on polyacrylamide gel + washing with toluene + drying at room temperature + refluxing with HCl for 4-6 h + washing with distilled water + drying at 70-75°C

- ***Glycidyl Methacrylate for binding of anionic metals***


Initiation with CAN on PVA-en-SC + maintaining pH 1-2
Addition of GMA at 35-40˚C + stirring under N2 atmosphere
Soxhlet extraction of reaction mixture with acetone and drying at 60-65˚C
Synthesis of intermediate Dissolving dried reaction mixture in DMF +D-glucose + NaCl + H2O + heating at 70-75°C for 10-12 h
Filtration & Washing with hot water + drying for 10- 12 h
Generation of Cationic Sites DMF + trimethylammonium chloride + NaCl + H2O + heating at 75-80˚C for 10- 12 h
Filtration, Washing & Drying at 50-55˚C for 10-12h

6. ***Spectroscopic and microscopic conformation of functionalization and adsorption process:***

FTIR Spectroscopy

Characterization of Active functional groups

Scanning Electron Microscopy

Characterization of Surface morphology

Thermo Gravimetric Analysis

Characterization of Environmental stability

Energy Dispersive X-ray spectroscopy

Characterization of the loaded metal on seed composite

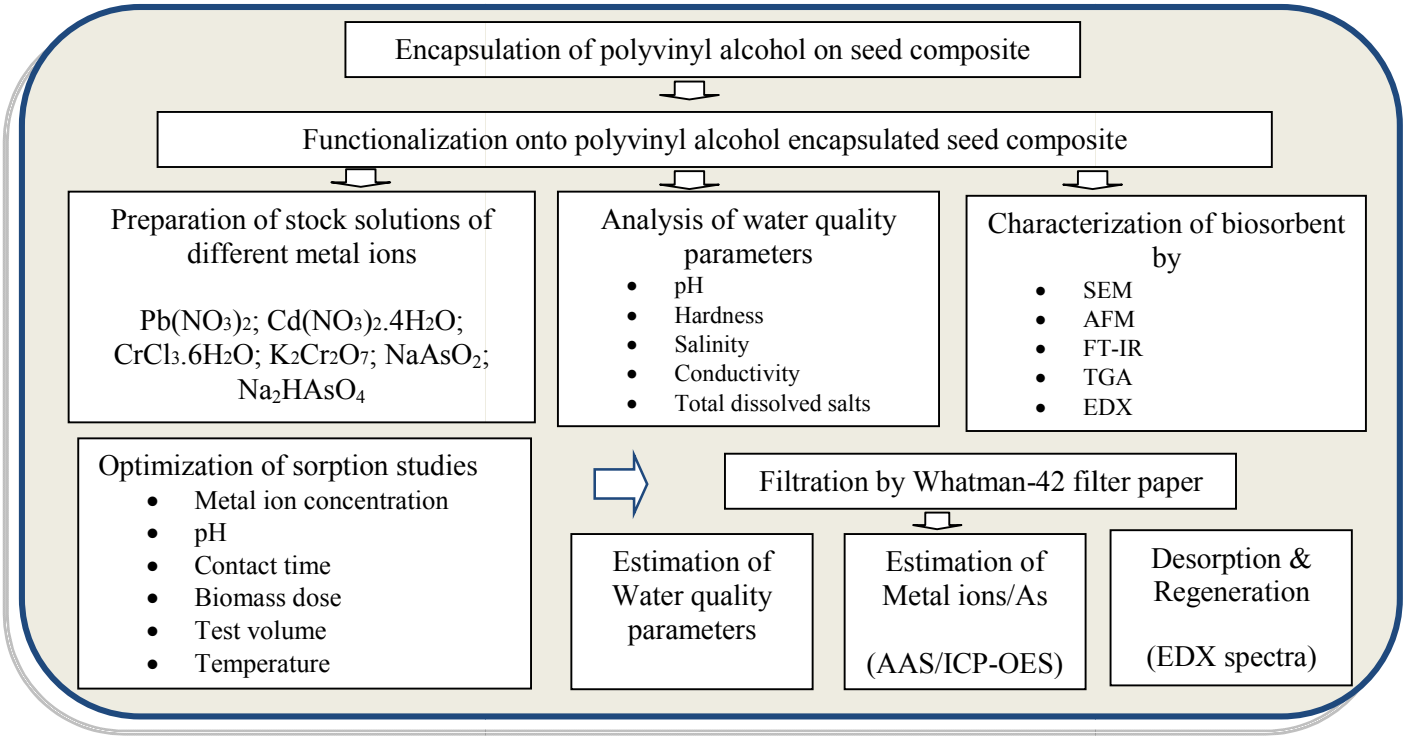
Atomic Force Microscopy

Characterization of Roughness of the seed composite

Atomic Absorbtion Spectroscopy/Inductively coupled plasma - optical emission spectrometry

For the estimation of metal ions/metalloid

An overview of the protocol of the process:



PRELIMINARY WORK DONE:

Sorption studies on reduction of physico-chemical parameters of water using native seed composite was carried out in batch experiment as a function of dosage (1.0-4.0 g), contact time (40 min) for 250 ml of water (tap water). The water sample was taken into Erlenmeyer flask, native seed composite was added and kept under magnetic stirring for 40 min. The sample was filtered and the filtrate was analyzed using pH meter, TDS meter and titration with EDTA. It was found that native seed composite dose (3g) was sufficient enough to normalize water check parameters reaching to the BIS standards of drinking water.

Table 5: Effect on various physico-chemical parameters of water before and after treatment with various doses of Native seed composite

S. No.	Parameters	Before Treatment	After treatment				BIS limits
			1 g	2 g	3 g	4 g	
1	pH	7.9	7.50±0.01	7.38±0.01	7.24±0.01	7.22±0.01	6.5-8.5
2	Hardness (mg/L)	800	724.66±1.52	535.00±1.21	505.33±0.57	500.00±0.52	200-600
3	TDS (mg/L)	2510	2278.33±7.64	1650.33±6.26	1586.66±2.88	1576.66±2.64	200-2000

(Source: IS 10500 : 2012)

SIGNIFICANCE OF THE WORK:

The research findings may be used for designing of a low cost domestic bio filter unit without any electrical consumption using seed composite having sorption and coagulation properties of proposed seed composite in conjunction with bio sand for the supply of drinking water free from toxic metals and with permissible values of turbidity, pH, salinity, total dissolved solids and hardness, particularly for rural and semi-urban areas of country.

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